Formation of dolomite and magnesite through hydrothermal alteration of Ca-carbonates: an experimental approach

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Introduction

Advanced knowledge about the physio-chemical conditions and reaction paths underlying Ca-Mg carbonate formation, such as dolomite and magnesite, during the advanced stage of diagenesis is a pre-requirement for the accurate interpretation of proxy signals established from carbonate-hosting sedimentary archives. In this study, hydrothermal precipitation experiments were performed in order to trace and quantify the evolution of elemental Ca, Mg and stable isotopic $\delta^{18}O$ signatures as well as the mineralogical phases during the (trans)formation of aragonite and low-Mg calcite to more stable dolomite and magnesite through intermediate, meta-stable Ca-Mg carbonate phases in the presence of Mg- and Na-chloride-rich brines. The evolution of reaction products and of the experimental solutions was monitored by ICP-OES, CRDS, FTIR, XRD, SEM and for alkalinity via titration.

Experimental setup and analyses

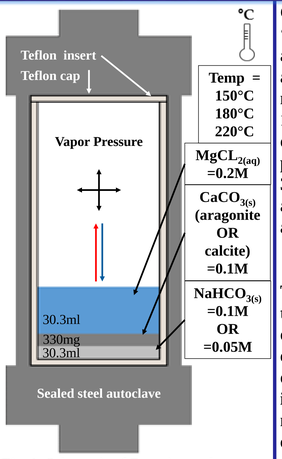


Fig. 1: Schematic of Experimental setup

Ca-Mg carbonates were synthesized in three experimental sets (hereby referred to as 'set-1', 'set-2', and 'set-3'). Each set of experiments were conducted within Teflon-lined stainless steel autoclaves through reaction of 330 mg (100 mmol.L^{-1}) of either inorganic calcite (set-1) or aragonite powder (set-2, set-3) with 30.3ml of an artificial brine solution containing 200 mmol.L^{-1} Mg and 100 mmol.L^{-1} NaHCO3 (set-1, set-2) or 50 mmol.L^{-1} (set-3) to {see Figure 1}. The artificial brine solution was highly depleted in ^{18}O ($\delta\,^{18}O_{VSMOW}$ = -46.3) to allow oxygen isotope exchange to be traced over the course of the experiment. Reactions were performed at temperatures of 150°C, 180°C and 220°C and were removed sequentially over 360 days total reaction time. Set-1 and set-2 had 30 reactors each with 15 reactors at 180°C and 15 at 220°C, set-3 had 45 total reactors which were divided to 15 at each 150°C, 180°C and 220°C.

The reactive fluid chemsitry of each experiment was measured by ICP-OES as well as titration for alkalinity. Mineralogy of each reaction solid was determined by Rietveld analysis of XRD spectra, stoichiometry of the Ca-Mg-carbonate phases was calculated using the equation $mol\%CaCO_3 = 333.33 \bullet d_{(104)} - 911.99$ *(Lumsden & Chimahusky, 1980)* and the degree of ordering of the dolomite phases was determined by the ratio of the $d_{(015)}/d_{(110)}$ peak intensities *(Kaczmarek and Sibley, 2011)*. The elemental composition of the bulk solid was also measured by ICP-OES of digested samples for the purpose of checking mass-balance between elemental concentrations and determined mineralogy. Both the reactive fluid and solid of each experiment were analyzed for their $\delta^{18}O$ composition.

Oxygen isotopes

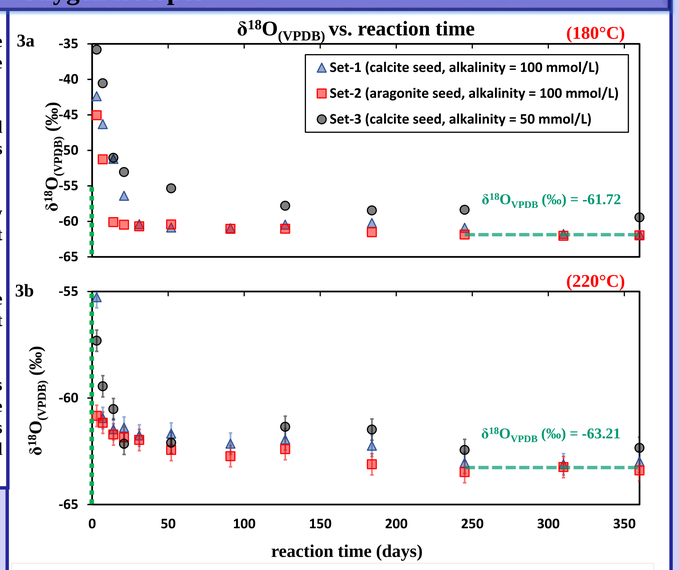
$\delta^{18}O$ evolution of the solids was successfully able to be traced due to the use of a highly ^{18}O-depleted reactive fluid

Experiments using aragonite seed material reached apparent equilibrium faster than equivalent experiments using a calcite seed.

Likewise, experiments with higher carbonate alkalinity reached apparent equilibrium faster than equivalent experiments at reduced alkalinity

There is an apparent offset in the $\delta^{18}O$ values where reduced alkalinity is used (values are 2-3‰ higher) at both 180°C and 220°C

The fractionation line for experimental solids supports existing experimental and theoretical values from the literature. It must be noted however that this fractionation line reflects a mixture of magnesite and dolomite



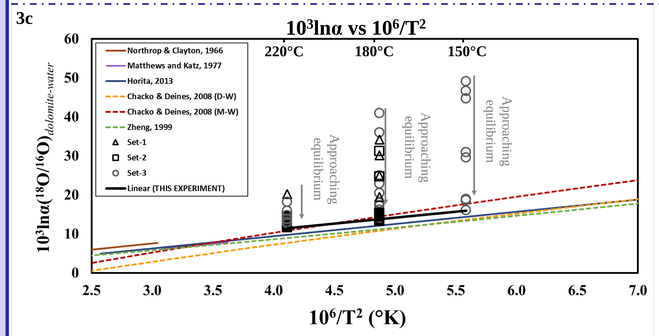


Fig. 3a: $\delta^{18}O$ vs. time at 180°C and 3b: $\delta^{18}O$ vs. time at 220°C. Vertical green-dotted lines indicate same range of $\delta^{18}O$ values, horizontal green dashed lines indicate approximate equilibrium state.
3c: $10^3 ln\alpha$ vs. $10^6/T^2$. solid lines represent experimental values, dashed lines represent theoretical values

Mineralogy

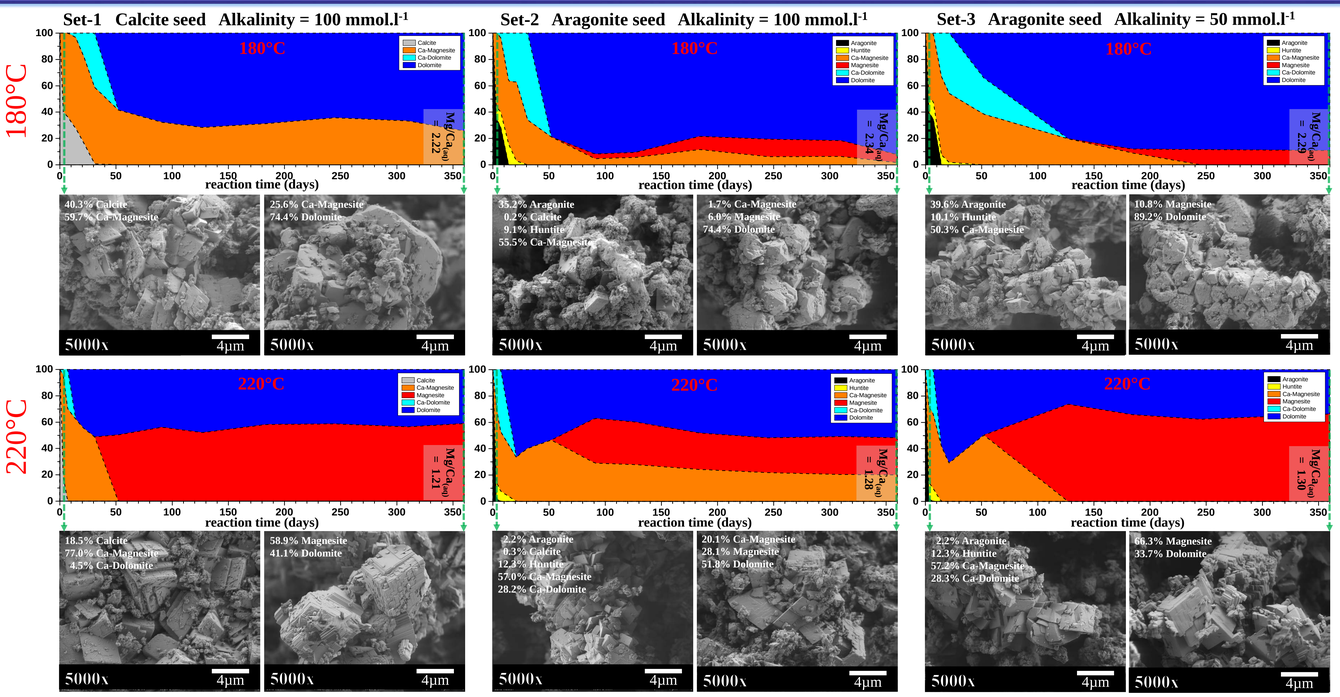


Fig. 2: Mineralogy plots and corresponding SEM images. Dotted green lines mark position of experiment SEM image was taken. For all plots the x-axis is reaction time (days) and the y-axis is is mineralogy (wt.%).

Based on the apparent solid-phase composition and reactive fluid chemistry, the following sequence of mineral growth was established:
→ Aragonite and/or low-Mg-calcite reacted with aqueous Mg2+ ions to form high-Ca-magnesite (+ huntite when coming from aragonite seed material)
→ Subsequent alteration of Ca-excess magnesite to Ca-excess dolomite and continued formation of Ca-excess magnesite
→ 'Step-ripening' of Ca-excess dolomite and magnesite phases towards their stoichiometric endmembers

Effect of temperature

- Final mineralogy and fluid composition across experiment sets -1, -2 and -3 similar at 180°C and at 220°C
- Under experimental conditions the system tends towards higher dolomite vs. magnesite formation at lower temperature
  - Unseen on this poster, experiment set-3 at 150°C resulted in a stable final mineralogy of 100% stoichiometric and highly ordered (0.70 – 0.92) dolomite
- Dissolution of initial intermediate Ca-rich-dolomite is faster at higher temperature

Effect of initial seed material

- Largest observable difference is that huntite is formed as an intermediate phase in experiments that used the aragonite seed material and not in experiments that used the calcite seed material
- Experiments at 220°C using the aragonite seed material experience an initial 'fast-growth' of stoichiometric dolomite at ~21 days of reaction time

Effect of alkalinity

- Experiments with reduced alkalinity (50 mmol.L^{-1} vs. 100 mmol.L^{-1}) result in a stable final composition of a mixture of near-stoichiometric- magnesite and dolomite. Experiments with higher alkalinity result in a greater Ca-content of the magnesite

Future work / What's next

- Geochemical modelling to recalculate pH to temperature
  → calculation of SI values for apparent mineral phases as function of reaction
  → examine fluid-rock relationship
- Separation of magnesite and dolomite in bulk solids via digestion with di-Na-EDTA
  → Oxygen, magnesium and calcium isotope measurements of individual phases
- Further experiments to observe evolution of $\delta^{18}O$ over the course of 1 month
  → Determination of pseudo first-order reaction rates for $\delta^{18}O$ exchange in magnesite and dolomite
- Alteration of calcite, aragonite, magnesite and dolomite crystals in $H_2{}^{18}O$
  → directly observe oxygen isotope exchange on the crystal surface via Raman spectroscopy